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Final Report for Phase I AFOSR STTR Project

**MULTIFUNCTIONAL NANOCOMPOSITE STRUCTURES VIA LAYER-BY-LAYER
ASSEMBLY PROCESS**

February 14, 2011

Sponsored by Air Force Office of Scientific Research

Proposal # F09B-T36-0241, topic AF09-BT36

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Title of Work: Multifunctional Nanocomposite Structures via Layer-by-Layer
Assembly Process

Reporting Period: 5/15/10 – 2/14/11

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EXECUTIVE SUMMARY

Current report is generated under Phase I STTR award on topic AF09-BT36. The overall goal of this project is to achieve large scale high-throughput manufacturing of multifunctional nanocomposites, which are comparable in physical characteristics to the standard aerospace composites, based on layer-by-layer (LBL) assembly process. To achieve this main objective, we proposed to: (1) construct and manufacture a new and fast LBL deposition machine (2) Realize exponential growth of LBL films with polyurethanes (PUs); (3) evaluate mechanical properties of the produced films; (4) manufacture large scale laminates of the free-standing films by consolidation. Using the new LBL deposition machine, dubbed '*Turbo LBL*', the deposition process was accelerated by *ca.* 100 times compared to traditional LBL deposition systems. The *Turbo LBL* system is compatible with a variety of nanomaterials and polyelectrolyte solutions which are typically used in traditional LBL assembly process. We demonstrated production of 10" x 40" size free standing LBL sheets at unprecedented rates, unattainable by conventional dip-dry LBL methods. Large size laminates of the free-standing LBL sheets made from graphene oxide (GO) and polyurethane (PU) polymers were fabricated. Mechanical property testing of the laminate samples indicated high extensibilities reaching 200%, and an overall excellent toughness. These promising results lay foundation for further optimization and their scale up manufacturing in Phase II.

RESULTS OBTAINED IN THE PROJECT

Task 1: Construction and manufacturing of a new LBL machine "Turbo LBL".

As described in the original proposal, the typical devices used in the deposition of LBL components sequentially transfer glass slides or other substrates from solution to solution. This system ultimately consists of adsorption of one component (eg. polymer), rinsing, drying, adsorption of another LBL component (eg. nanotubes), and another rinsing and drying steps. This approach of fabrication of LBL coatings and free-standing films require substantial amount of time. As a result, our task was to eliminate this problem by designing and constructing a continuous LBL deposition machine that will not only significantly accelerate the rate of deposition, but also produce films with comparable physical characteristics as observed from the conventional methods. The initial design schematics is depicted in Figure 1. On this fundamental idea, *Turbo LBL* machine was designed and developed applying an entirely new technology of LBL systems using proprietary know-how of *Nico Technologies* personnel.

During the project time period preceding this report, we designed and constructed two *Turbo LBL* machines, which are identified as *Turbo LBL 1* and *Turbo LBL 2*. They are similar in concept but different in capacity and operations of the nozzles. *Turbo LBL 2* is more advanced and most of the results will be referred to this latest design of the hardware. The heart of both *Turbo LBL* deposition systems is a rotating cylindrical substrate, or a drum (Figure 1). The latter rotates around the vertical axis while the aqueous dispersions/solutions are sprayed from the stationary nozzles positioned in four quadrants around the drum. The quadrants are separated by the spray shields and air-knives to avoid the transfer of the mist from adjacent quadrants. As the drum rotates a vertical section of its surface is sprayed by polymer solution, water, nanoparticle solution, and water again, thereby repeating the characteristic sequence of the LBL deposition but without time-consuming transfer of the substrate from one beaker to another. *Turbo LBL* has some similarities with existing spray-LBL systems but they utilize alternate spraying. For instance, a flat surface is

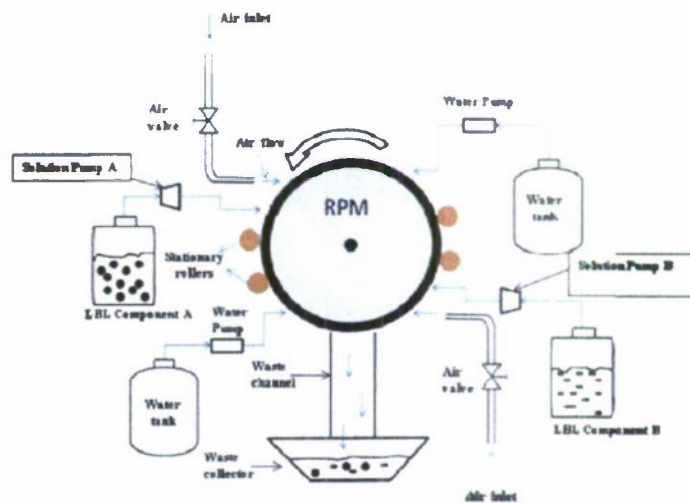


Figure 1. Original schematics of Turbo LBL 1 (top view).

sprayed first with a solution of a polymer for a certain period of time, and then the same surface is sprayed with water for some period of time, nanoparticles, and water again. Alternate spray systems result in faster deposition rates than traditional LBL, but they are still relatively time consuming and often give poor uniformity of the coatings. Our system utilizes *continuous spray* without interruptions, which makes possible acceleration of the deposition in respect to the alternate spray systems by, at least 8 times. The multiple nozzles distributed along the vertical axis of the cylindrical substrate in *Turbo LBL* and air knives between the quadrants provide highly uniform multilayers.

Our hardware solutions eliminate complicated robotic devices and provide continuous deposition of LBL composites. Additionally, *Turbo LBL* system has only one moving part, and for that reason, is exceptionally reliable and easy to maintain.

Task 1-1. Testing of performance of Turbo LBL

Typically, the substrate of choice is held firmly onto the central drum and held in place with a hose-clamp. We tested various substrates such as Teflon, polycarbonate, and fabrics (Figures 2 and 3). The solution and water pumps are easily regulated to desired flow rates. Steady compressed air flow provided through the air blades facilitates drying after rinsing with water. Free-standing LBL films can be easily produced from LBL colloidal and polyelectrolyte solutions typically used in the conventional dipping LBL method when assembled on Teflon substrate (Figures 2). The surface of the substrate can be pre-treated by deposition of thin film of cellulose acetate to enhance adsorption of the initial LBL components. After deposition, the LBL film can be detached easily with slight application of acetone (for polycarbonates) or without (as with Teflon).

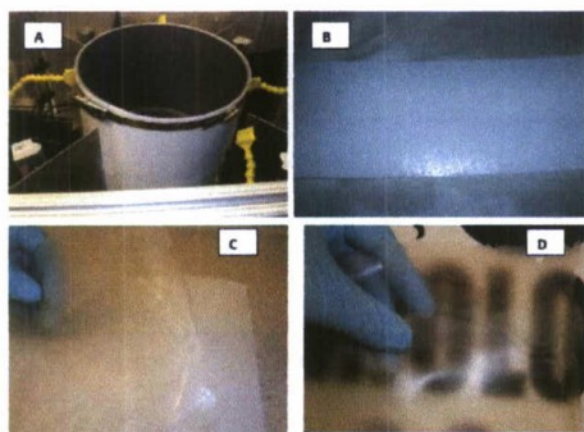


Figure 2. Photographic images of (A) LBL coating of PDPA-PAA on Teflon substrate on TurboLBL2. (B) PDPA-PAA LBL coating (100 bilayers) on Teflon. (C) Detachment of LBL film. (D) The free standing PDPA-PAA LBL film.



Figure 3. (A) LBL coating of Kevlar fabric using. (B) Clay-polymer coated Kevlar fabrics. (C) 10" x 40" LBL sheet made on Turbo LBL machine. (D) SEM image of surface of the coated Kevlar fabric.

Task 2. Realization of exponentially growing LBL films and preparation of large size LBL sheets.

Free standing LBL sheets were made from polyurethane (PU) and polyacrylic acid (PAA) solutions (1wt.%), both of which are known exponential LBL polyelectrolytes. A method of incorporating nanomaterials [eg. clay nanosheets, silica (SiO_2) nanoparticles, and graphene oxide (GO) nanosheets] to the LBL films was realized by mixing the PAA solution with the nanocolloids yielding a homogenous solution mixture. The large-size free-standing LBL sheets were build-up on polycarbonate substrate (Figure 4B). To facilitate better adhesion of the LBL

films, the substrate was coated with two bilayers of poly(diallyl dimethylammonium) chloride [PDDA] and PAA. This approach also enables easy detachment of the LBL sheets (Figure 4B). The substrate is then simply washed with water and can be re-used for further LBL film production. The combination of exponential LBL, spraying and high-speed rotation mechanism of Turbo LBL makes for the fast LBL film fabrication. We obtained several LBL

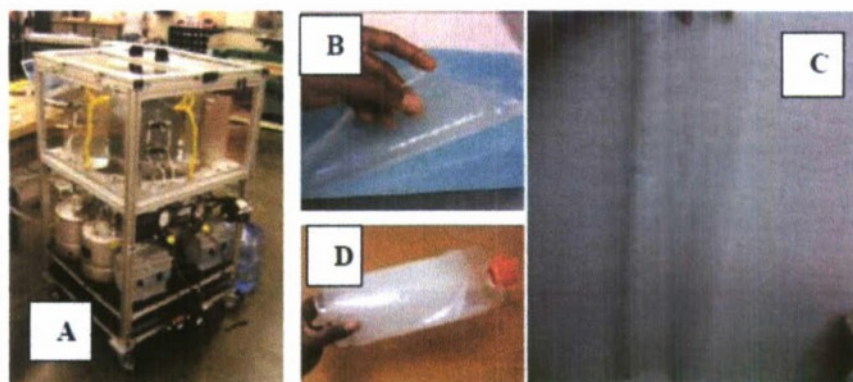


Figure 4. Photographs of (A) Turbo LBL2; (B) detachment of PU/PAA(clay)₃₀ LBL sheet; (C) the 9"x 40" free-standing LBL sheet; (D) demonstration of robustness and flexibility of the LBL sheet – wrapping around a 4 inch diameter.

coatings and free-standing films with thicknesses reaching 450 μm in *ca.* 30 minutes at speed of 2RPM. It would have taken more than from 10 to 500 hours to reach similar thickness of LBL films with the conventional dip-dry devices at their optimal deposition speeds depending on the deposition system used.

GO was synthesized following modified Hummer's method¹ (Figure 5A). GO nanosheets can be assembled in LBL structures with exponential and non-exponential LBL polyelectrolytes (Figure 5B). The GO LBL nanocomposites reveal some fascinating properties as seen in the thermal expansion plots (Figure 5C). At

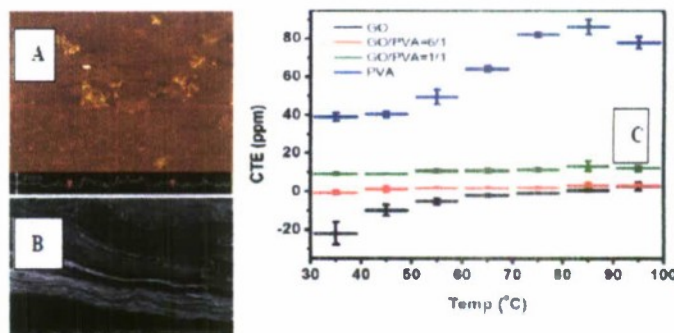


Figure 5. (A) AFM image of GO nanosheets; (B) Cross-section SEM image of GO/PVA nanocomposites (6:1); (C) CTE plots at different GO/PVA ratios.

given ratios, the coefficient of thermal expansion (CTE) of the GO/PVA nanocomposite, for example, remains virtually unchanged. Such a unique property can be very valuable in several structural aerospace applications.

Task 3: Evaluation of mechanical properties of GO/PU films.

The mechanical testing of the GO composite sheets (Fig. 3C) and laminates (Fig. 7) were carried out using Instron Q Systems model 100 (Test Resources) on small sample strips of width < 1.5 mm. Figure 6 and table 1 show mechanical testing data of the GO composites and comparison

with some conventional aerospace structural materials. The toughness (K) of the GO composite was calculated to be $\sim 52 \text{ MJ/m}^3$ with elongation at break of 200%. The toughness recorded here is more than 27 times higher than previously reported value for toughness of GO-polyelectrolyte LBL multilayers (1.9 MJ/m^3) and with elongation at only 20%.² It is also more than 70 times higher

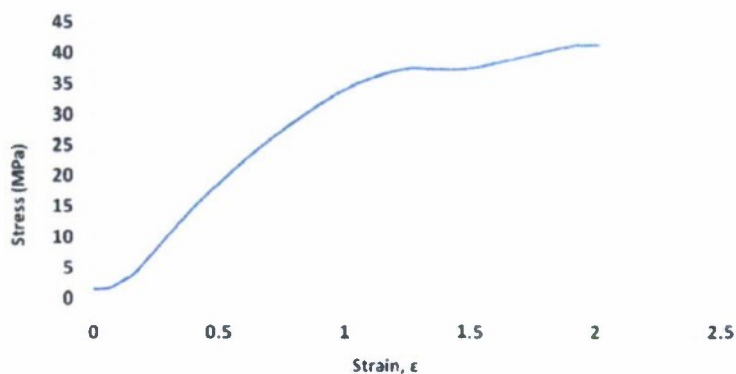


Figure 6. (A) Representative stress-strain curve for the GO composite.

than the values reported for LBL nanocomposites reinforced with metal nanowires and nanoparticles^{3,4}, as well as silk-clay composites.⁵

Materials	Tensile strength (MPa)	Young's Modulus	Elongation at break (%)	Specific gravity (g/cm^3)
GO-PU composite (Nico Tech & UM)	42	45 MPa	200	1.5
Aluminum alloy 1199-0	45	60-70 GPa	50	2.7
Airex® C70 Structural Foam	7.5	230 MPa	8-20	0.04
Balsa Wood Core (Baltek® SB)	75	1130-6000 GPa	-	0.13
Polycarbonate sheet (McMaster-Carr)	33	185 MPa	204	1.2
Nylon	86	2.8 GPa	90	1.14

Table 1. Comparison of mechanical properties with some conventional materials.

Current GO composites possess impressive toughness and strain far exceeding any graphene oxide composite reported so far. The relatively low tensile strength value is attributable to the inherent structural nature of the individual composite sheets which reveal a porous internal network (Figure 7B inset). The ductile nature of the GO composite can be due to the PU backbone.⁶ Incorporation of cross-linking inorganic or organic moieties in the GO composite matrix can potentially enhance the tensile strength.⁷

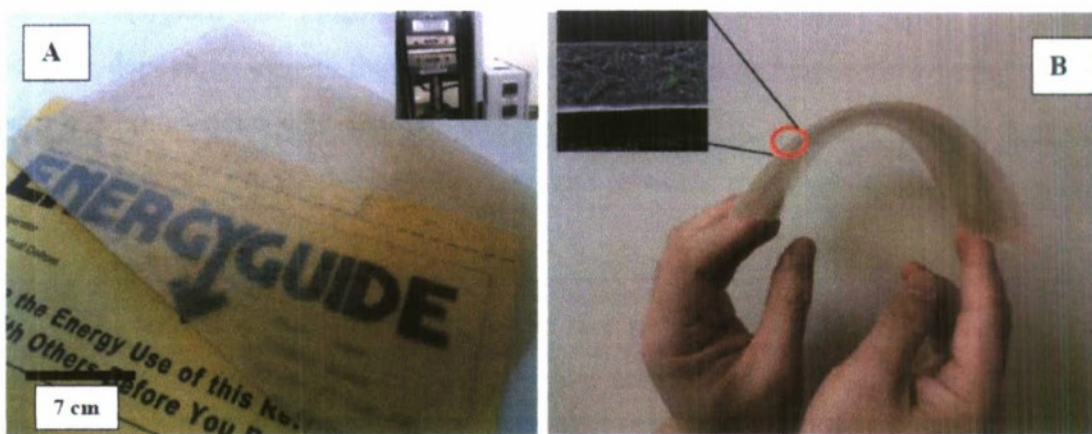


Figure 7. Photographic images of (A) GO LBL composite laminate coupons. Each coupon comprises of 5 LBL sheets. Inset shows the lamination process using Carver Hydraulic Unit 3912. The sheets are sandwiched between two Teflon slabs and hot-pressed for 40 minutes. (B) Demonstration of flexibility of the laminate coupons. Inset shows the cross-section SEM image.

Task 4: Preparation of large scale laminates by consolidation.

Consolidation was achieved via hot-pressing of individual free-standing LBL sheets made by *Turbo LBL 2* (Figure 7A inset). No adhesive was needed to achieve excellent lamination of the prepared composites

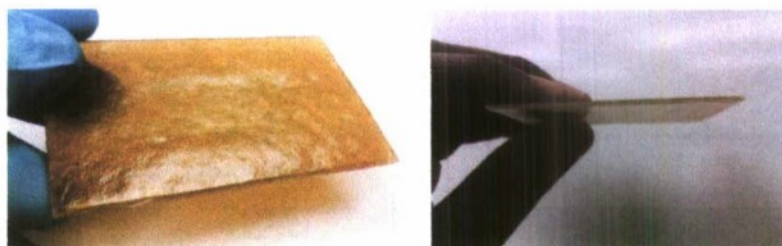


Figure 8. Photographic images of representative GO composite laminate coupon (4" x 6" x 2 mm).

due to the elasticity of the material imparted by poly(urethane), PU, utilized as one of the LBL partners for GO nanosheets. With *Turbo LBL* deposition system and consolidation technology demonstrated, LBL composites definitely transcend the realm of microscale devices into the realm of high performance macroscale components. This achieved objective demonstrated that GO composite materials with impressive mechanical properties can be made in both large sizes and thicknesses (Figure 8), thereby paving the way for their further optimization and development.

CONCLUSIONS AND RECOMMENDATIONS FOR PHASE I

In the time period since commencement of this Phase I project, we have accomplished the following milestones/objectives:

Milestone 1: Designed and constructed a continuous LBL deposition system. A robust and versatile LBL deposition system that allows application of up to four different LBL solution or polyelectrolyte components was designed and manufactured. The new LBL system demonstrates a fast, high-throughput, environmentally benign, and low-cost manufacturing technique for LBL composite sheets with tailored properties.

Milestone 2: Demonstrated production of large size LBL sheets exceeding all reported LBL multilayers made by conventional techniques. We achieved LBL deposition on a variety of substrates including fabrics, polycarbonate and Teflon. The detached LBL sheets measured up to 10" x 40", which is greater than all reported free-standing films made from polymers or composite materials by any of the conventional techniques. The dimensions of the LBL materials made now are sufficiently large to manufacture many parts of unmanned aerial vehicles (UAVs) or some fairly small but critical parts of conventional planes

Milestone 3: Realized highest toughness value for GO composite reported so far. The impressive results obtained in Phase I lay the pathway for optimization of structure and deposition conditions that will yield substantially better results in Phase II.

Milestone 4: Realized consolidation of LBL sheets in large sizes.

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Dear Officer,

Please find enclosed two copies of the Final Technical Report on the Phase I STTR AFOSR Project titled "Multifunctional nanocomposite structures via layer-by-layer assembly process", contract # FA9550-10-C-0129.

Sincerely,

A handwritten signature in blue ink, appearing to read "Elvira Stesikova", written in a cursive style.

3/5/2011

Elvira Stesikova, PhD, MBA
Project Manager
Nico Technologies Corp.